Temperature dependent magnetic anisotropy in metallic magnets from an ab-initio electronic structure theory: $L1_0$-ordered $FePt$

J.B.Staunton[1], S.Ostanin[2], S.S.A.Razee [3], B.L.Gyorffy [4], L.Szunyogh [5], B.Ginatempo[6] and Ezio Bruno[6]

[1]*Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.*
[2] *Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, U.K.*
[3]*Department of Physics, Kuwait University, P.O. Box 5969, SAFAT 13060, Kuwait*
[4] *H.H.Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, U.K.*
[5] *Department of Theoretical Physics, Budapest University of Technology and Economics, Budapest, Hungary and*
[6] *Dipartimento di Fisica and Unita INFM, Universita di Messina, Sicily, Italy*
(Dated: February 2, 2008)

On the basis of a first-principles, relativistic electronic structure theory of finite temperature metallic magnetism, we investigate the variation of magnetic anisotropy, K, with magnetisation, M, in metallic ferromagnets. We apply the theory to the high magnetic anisotropy material, $L1_0$-ordered FePt, and find its uniaxial K consistent with a magnetic easy axis perpendicular to the Fe/Pt layering for all M and to be proportional to M^2 for a broad range of values of M. For small M, near the Curie temperature, the calculations pick out the easy axis for the onset of magnetic order. Our results are in good agreement with recent experimental measurements on this important magnetic material.

By accounting for relativistic effects such as spin-orbit coupling on electronic structure, recent 'first-principles' theoretical work has been successful in describing trends in the magnetocrystalline anisotropy (MCA) of magnetic materials. [1, 2, 3] This is useful for the understanding of permanent magnetic properties, domain wall structure, magnetic nanostructures etc. One aspect, however, which has received scant attention from such ab-initio theories is its temperature dependence. Modelling this phenomenon seems to rest largely on the seminal papers by Callen and Callen and others [4] published nearly 40 years ago which focussed on the temperature dependence associated with single ion magnetic anisotropies. In this letter we investigate how far this approach can be justified for metallic magnets on the basis of a first-principles, material specific, parameter-free theory of how the magnetocrystalline anisotropy depends on temperature. The proposed theory involves a detailed, relativistic description of the electronic structure and hence it includes a complete desciption of the spin-orbit coupling. The thermally induced magnetic fluctuations are taken into account by a relativistic generalisation of the, by now well-tried, disordered local moment (DLM) picture. [5, 6]

The topic has recently received extra impetus from extensive experimental studies of magnetic films and nanostructures and their technological potential. For example, the recent fabrication of assemblies of smaller and smaller magnetic nanoparticles holds considerable promise for the design of ultra-high density magnetic data storage media. [7] But this is hampered by a particle size limit set so that thermally driven demagnetisation and loss of data is avoided over a reasonable storage period. This limit can be lowered by using materials with high magnetocrystalline anisotropy, K, since the superparamagnetic diameter of a magnetic particle is proportional to $(k_B T/K)^{\frac{1}{3}}$, where $k_B T$ is the ther-

mal energy. [8] In this context, the chemically ordered $L1_0$ phase of equiatomic $FePt$, which has high uniaxial MCA (4-10 10^7 ergs/cm^3 or up to 1.76 meV per $FePt$ pair [9, 10]), has been subjected to much attention and arrays of $FePt$ nanoparticles with diameters as small as 3 nm have been synthesised. [7, 11] A way to write to media of very high K material is by temporary heating. [12, 13, 14] The magnetocrystalline anisotropy is reduced significantly during the magnetic write process and the information is locked in as the material cools. Modelling this process and improving the design of high density magnetic recording media therefore requires an understanding of how K varies with temperature.

So for the first application of our theory we have chosen $L1_0$-ordered $FePt$. Given its technological potential there have recently been some careful experimental studies of its fundamental magnetic properties. [11, 12, 15] These show a strong temperature dependence to K. We find good agreement with these data. In particular we find $K(T) \propto (M(T)/M(0))^2$ over a broad magnetisation range, in line with the results reported in two of these three studies. [12, 15] Notably the low temperature behavior is qualitatively different from that of the single-ion anisotropy models used over many years. [4]

The magnetic anisotropy of a material can be conveniently expressed as $K = \sum_\gamma k_\gamma g_\gamma(\hat{n})$ where the k_γ's are magnetic anisotropy constants, $\hat{n}$ is the direction of the magnetisation and g_γ's are polynomials (spherical harmonics) of the angles θ, ϕ describing the orientation of $\hat{n}$ and belong to the fully symmetric representation of the crystal point group. For a uniaxial ferromagnet such as $L1_0$-ordered $FePt$, $K = k_0 + k_2(\cos^2\theta - 1/3) + \cdots$.

As the temperature rises, K decreases rapidly. The key features of the results of the early theoretical work on this effect [4] are revealed by a classical spin model pertinent to magnets with localised magnetic moments.

The anisotropic behavior of a set of localised 'spins' associated with ions sitting on crystalline sites, i, in the material, is given by a term in the hamiltonian $H_{an} = \sum_i \sum_\gamma k_\gamma g_\gamma(\hat{s}_i)$ with $\hat{s}_i$ a unit vector denoting the spin direction on the site i. As the temperature is raised, the 'spins' sample the energy surface over a small angular range about the magnetisation direction and the anisotropy energy is given from the difference between averages taken for the magnetisation along the easy and hard directions. If the coefficients k_γ are assumed to be rather insensitive to temperature, the dominant thermal variation of K for a ferromagnet is given by $K(T)/K(0) = \langle g_l(\hat{s})\rangle_T/\langle g_l(\hat{s})\rangle_0$ The averages $\langle \cdots \rangle_T$ are taken such that $\langle \hat{s} \rangle_T = M(T)$, the magnetisation of the system at temperature T, and l is the order of the spherical harmonic describing the angular dependence of the local anisotropy i.e. $l = 2$ and 4 for uniaxial and cubic systems respectively. At low temperatures $K(T)/K(0) \approx (M(T)/M(0))^{l(l+1)/2}$ and near the Curie temperature T_c, $K(T)/K(0) \approx (M(T)/M(0))^l$. These features are borne out rather well in magnets where the magnetic moments are well-localised, e.g. rare-earth and oxide magnets, but it is questionable whether such an analysis should hold for itinerant ferromagnets. [8] Here, we examine these issues in the context of the $L1_0$-ordered FePt intermetallic compound for which careful experiments [12, 15] find $K(T)/K(0) = (M(T)/M(0))^n$,where $n = 2$ instead of $n = 3$, over a large temperature range. As will be shown presently, our ab-initio calculations are in good agreement with this surprising result.

Magnetocrystalline anisotropy is caused largely by spin-orbit coupling and receives an ab-initio description from the relativistic generalisation of spin density functional (SDF) theory. [1] Up to now calculations of the anisotropy constants K have been suited to $T = 0K$ only. They treat the spin-orbit coupling effects using either perturbation theory [3] or a fully relativistic one [2, 16]. Typically the total energy, or the single-electron contribution to it (if the force theorem is used), is calculated for two or more magnetisation directions, $\hat{n}_1$ and $\hat{n}_2$ separately, i.e. $E_{\hat{n}_1}$, $E_{\hat{n}_2}$, and then the MCA is obtained from the difference, ΔE. Since the MCA is a small part of the total energy of the system, in many cases of the order of μeV, it is numerically more precise to calculate the difference directly [16] so that $\Delta E = -\int^{E_{F_1}}[N(\varepsilon; \hat{n}_1) - N(\varepsilon; \hat{n}_2)]d\varepsilon - \frac{1}{2}n(E_{F_2}; \hat{n}_2)(E_{F_1} - E_{F_2})^2 + \mathcal{O}(E_{F_1} - E_{F_2})^3$ where E_F^1, E_F^2 are the Fermi energies when the system is magnetised along the directions $\hat{n}_1$ and $\hat{n}_2$ respectively and $n(\varepsilon; \hat{n})$ and $N(\varepsilon; \hat{n})$ are the density of states and integrated density of states respectively. We have used this rationale with a fully relativistic theory to study the MCA of magnetically soft, compositionally disordered binary and ternary component alloys [16, 17], the effect upon it of atomic short-range order [2] and recently its dependence in $FePt$ upon the extent of $L1_0$ long range chemical order [18].

There are a number of calculated values of the MCA of completely $L1_0$-ordered $FePt$ at $T = 0K$ in the literature [19] ranging from 1.2 to 3.9 meV (7-22 10^7) ergs/cm^3. K for $FePt$ has been measured at room temperature [9] to be 6.6 10^7ergs/cm^3 although more recent measurements [10] suggest that this value could exceed 10^8ergs/cm^3 for completely ordered $FePt$. The easy axis in both experiment and theory is along the c-axis, $(0,0,1)$, perpendicular to the Fe and Pt layers.

Our calculations of the MCA of materials use spin-polarised, relativistic multiple scattering theory and an adaptive mesh algorithm [20] for Brillouin zone integrations such that the numerical precision of our calculations is to within 0.1 μV. [2, 16] These attributes are also important for the theoretical calculations of the temperature dependence of the MCA described below. We calculate the MCA of ordered FePt at $T = 0$K to be 1.696 meV. We start from a self-consistent field, scalar relativistic calculation (atomic sphere approximation) of the electronic structure and effective potentials for the Fe and Pt sites. We then perform a further fully relativistic electronic structure calculation, recalculate the Fermi energies E_F^1 and E_F^2 and determine the MCA. For $L1_0$-ordered FePt we find that if E_F^1 and E_F^2 are artificially changed by a small amount, the MCA varies significantly. For example, the MCA jumps from 1.696 to 2.751 meV if the E_F's are lowered by just 0.2 eV. This sensitivity may explain, in part, the range of published values of the MCA of FePt. We can also deduce that the magnetic anisotropy of this strong permanent magnet might be further enhanced by replacing a few atomic percent of Pt with Ir.

In a metallic ferromagnet at $T = 0$K the electronic band structure is spin-polarised. With increasing temperature, spin fluctuations are induced which eventually destroy the long-range magnetic order and hence the overall spin polarization of the system's electronic structure. These collective electron modes interact as the temperature is raised and are dependent upon and affect the underlying electronic structure. For many materials the magnetic excitations can be modelled by associating local spin-polarisation axes with all lattice sites and the orientations $\{\hat{e}_i\}$ vary very slowly on the time-scale of the electronic motions. [5] These 'local moment' degrees of freedom produce local magnetic fields on the lattice sites which affect the electronic motions and are self-consistently maintained by them. By taking appropriate ensemble averages over the orientational configurations, the magnetic properties of a system can be determined and, with the explicit inclusion of relativistic effects upon the electronic structure, the temperature dependence of the MCA can be obtained.

Consider this DLM picture of a ferromagnetic metal magnetised along a direction $\hat{n}$ at a temperature T. The probability that the system's local moments are configured according to $\{\hat{e}_i\}$ is

$$P^{(\hat{n})}(\{\hat{e}_i\}) = \exp[-\beta\Omega^{(\hat{n})}(\{\hat{e}_i\})]/Z^{(\hat{n})} \qquad (1)$$

where the partition function $Z^{(\hat{n})} = \prod_j \int d\hat{e}_j \exp[-\beta\Omega^{(\hat{n})}(\{\hat{e}_i\})]$. $\Omega^{(\hat{n})}(\{\hat{e}_i\})$ is the 'generalised' electronic grand potential from SDFT [6] and $\beta = (k_B T)^{-1}$. The thermodynamic free energy, which accounts for the entropy associated with the orientational fluctuations as well as creation of electron-hole pairs, is given by $F^{(\hat{n})} = -k_B T \log Z^{(\hat{n})}$. The role of a local moment hamiltonian, albeit a highly complicated one is played by $\Omega\{\hat{e}_i\}$. By choosing a suitable reference 'spin' hamiltonian $\Omega_0\{\hat{e}_i\} = \sum_i h^{(\hat{n})}\hat{n}\cdot\hat{e}_i$ and, using the Feynman Inequality [21], a mean field theoretical estimate of the free energy is obtained, [6]

$$F^{(\hat{n})} = \langle\Omega^{(\hat{n})}\rangle + (1/\beta)\sum_i \int P^{(\hat{n})}(\hat{e}_i)\ln P^{(\hat{n})}(\hat{e}_i)d\hat{e}_i \quad (2)$$

where the probability of a moment pointing along $\hat{e}_i$ on a site i is

$$P^{(\hat{n})}(\hat{e}_i) = \frac{\exp[-\beta h^{(\hat{n})}\hat{n}\cdot\hat{e}_i]}{\int \exp[-\beta h^{(\hat{n})}\hat{n}\cdot\hat{e}_i]d\hat{e}_i} \quad (3)$$

and the Weiss field at a site is given by

$$h^{(\hat{n})} = \frac{3}{4\pi}\int \langle\Omega^{(\hat{n})}\{\hat{e}_l\}\rangle_{\hat{e}_i}\hat{n}\cdot\hat{e}_i d\hat{e}_i. \quad (4)$$

where $\langle\cdots\rangle_{\hat{e}_i}$ denotes a constrained statistical average with the magnetic moment on site i being fixed along $\hat{e}_i$.

The magnetisation $\mathbf{M} = M\hat{n}$ is given by $M = \mu\int P^{(\hat{n})}(\hat{e}_i)\hat{n}\cdot\hat{e}_i d\hat{e}_i$. μ is the size of the local moment on the site and is determined self-consistently. [6] For materials where this DLM picture is suitable, the sizes of the local moments, μ, remain fairly constant so that even in the paramagnetic state where $M = 0$, the μ's are roughly the same as the magnetic moment per atom in the ferromagnetic state at $T = 0$K. In a first-principles implemenation of such a DLM picture, the averaging over the orientational configurations of the local moments is performed using the KKR-CPA method adopted from the theory of random metallic alloys. [6, 22] Using this methodology over the past 20 years, the paramagnetic state, onset of magnetic order and transition temperatures of many systems have been successfully described. [23] All applications to date, however, have neglected relativistic effects and have been devoted to the paramagnetic state where the symmetry turns the calculation into a binary alloy-type one with half the moments oriented along a direction and the rest antiparallel. Once relativistic effects are included and/or the ferromagnetic state is considered, this simplicity is lost and the continuous probability distribution $P^{(\hat{n})}(\hat{e}_i)$'s must be sampled for a fine mesh of angles and the averages with the probability distribution performed numerically. (Careful checks have to be made to ensure that the sampling of $P^{(\hat{n})}(\hat{e}_i)$ is sufficient - in our calculations some 25,000 values were used.) In the ferromagnetic state, the magnetic anisotropy is given by the difference between the free energies, $F^{(\hat{n})}$, for different

magnetisation directions, $\hat{n}$, but the same magnetisation M.

Once again our study of $FePt$ starts with a self-consistent, scalar-relativistic calculation, this time for the paramagnetic (DLM) state. On the Fe sites a local moment of 2.97 μ_B is set up whilst no moment forms on the Pt sites. For the same lattice spacings ($c = 0.385$nm, $c/a = 1$), we found that, for the completely ferromagnetically ordered state of $FePt$ at $T = 0$K, the magnetisation per Fe site is 2.93 μ_B and a small magnetisation of 0.29 μ_B is associated with the Pt sites. This suggests that the thermal effects on the magnetic properties should be well-described by the DLM picture. Using the self-consistent potentials and magnetic fields of the paramagnetic DLM state, we proceed by picking a series of values of $M(T)/M(0)$ to set the probabilities, $P^{(\hat{n})}(\hat{e}_i)$. By calculating $\langle\Omega^{(\hat{n})}\{\hat{e}_l\}\rangle_{\hat{e}_i}$, using our relativistic DLM method, we find the Weiss field, $h^{\hat{n}}$, at each value and for a given $\hat{n}$, and hence determine the temperature dependence of the magnetisation. The results are shown in Figure 1. Although the shortcomings of the mean field approach do not produce the spinwave $T^{\frac{3}{2}}$ behavior at low temperatures, the easy axis for the onset of magnetic order is obtained ($h^{(001)} > h^{(100)}$ as $T \to T_c$) and it corresponds to that found at lower temperatures both experimentally and in all theoretical ($T = 0$K) calculations, perpendicular to the Fe, Pt layer stacking. (A straightforward adaptation of this approach to other systems such as thin films in combination with $T = 0$K calculations may be useful in understanding temperature induced spin reorientation transitions.) A Curie temperature of 935K is found, in fair agreement with the experimental value of 750K. [6, 24]
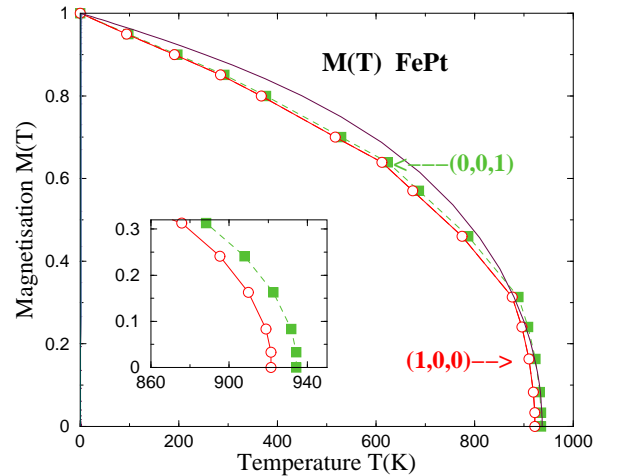

FIG. 1: The magnetisation of ordered FePt as a function of temperature. The filled squares refer to a magnetisation along $\hat{n} = (0, 0, 1)$ whilst the open circles refer to $\hat{n} = (1, 0, 0)$. The onset of magnetic order occurs at 935K along the easy axis, $(0, 0, 1)$. The full line shows the magnetisation from the mean field approximation to a classical Heisenberg model for comparison. The inset shows the region near the onset.

The free energy difference, $F^{(0,0,1)} - F^{(1,0,0)}$, i.e. the magnetocrystalline anisotropy, $K(T)$, is also calculated using the theory and leads to the key results of this letter shown in Figure 2. At $T = 0K$, the MCA has a value -1.740 meV, close to the value, -1.696 meV, obtained by the earlier, separate calculation for this situation for the completely ferromagnetic state. Figure 2 shows the MCA, $K(T)$, versus $M(T)/M(0)$. Curves for the single-ion classical spin model anisotropy [4] and $(M(T)/M(0))^2$ are also shown for comparison. Apart from near complete magnetisation, $0.9 < M(T)/M(0) < 1$, our results show a good approximate $(M(T)/M(0))^2$ behavior in good agreement with experiment. [12, 15]. This is in marked contrast to the model, which becomes proportional to $(M(T)/M(0))^3$ for the larger $M(T)$'s.
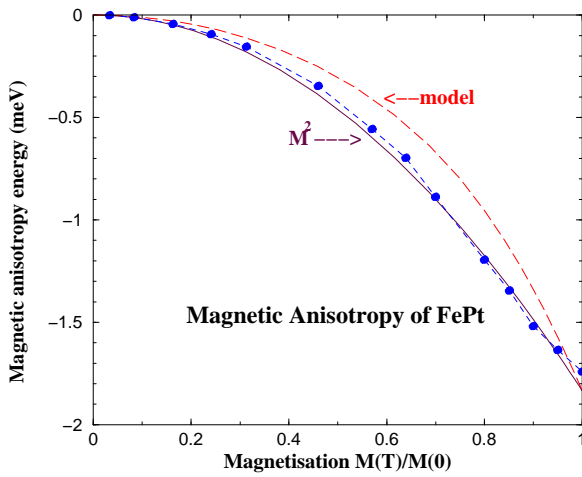

FIG. 2: The magnetic anisotropy of FePt as a function of magnetisation. The filled circles show the calculations from the ab-initio theory. The full line show $K_0(\frac{M(T)}{M(0)})^2$ and the dashed line shows the single-ion model function $K_0\frac{<g_2(\hat{e})>_T}{<g_2(\hat{e})>_0}$ with K_0 = -1.835 meV.

Evidently Figure 2 shows that at low temperatures in the single ion model the MCA falls off much more quickly as the temperature is increased and the overall magnetisation is reduced. Moreover our theory for an itinerant electron system does capture the behavior of the K versus magnetisation relation quantitatively. This theory assumes that there is a separation between fast and slow electronic degrees of freedom. A picture of 'local moments' emerges naturally but with a subtlety that their existence and behavior are determined by the fast electronic motions. We expect the MCA of the important magnetic materials $L1_0$-CoPt and FePd to follow a similar variation with magnetisation since the local moments sustained on the Co and Fe sites in the paramagnetic DLM states (1.78 and 2.98 μ_B respectively) are comparable in size to magnetisation per site in the completely ferromagnetic states (1.91 and 2.96 μ_B). Our DLM theory should therefore have good prospects in describing the variation of K with magnetisation for a range of metallic magnets like these. The success of the above relativistic DLM methodology in explaining the unexpected behavior of $L1_0$- $FePt$ suggests that further calculations for promising magnetic materials in bulk, thinfilms or in magnetic nanostructures may be valuable for the future modelling and exploitation of their magnetic properties.

[1] H.J.F.Jansen, Phys. Rev. B **59**, 4699 (1999).
[2] S.S.A.Razee *et al.*, Phys. Rev. Lett. **82**, 5369, (1999).
[3] e.g. T.Burkert *et al.*,Phys. Rev. B **69**, 104426 (2004); A.B.Shick *et al.*, Phys. Rev. B **56**, R14259, (1997).
[4] H.B.Callen and E.Callen, J.Phys.Chem.Solids, **27**, 1271, (1966); N.Akulov, Z. Phys. **100**, 197, (1936); C.Zener, Phys. Rev. B**96**, 1335, (1954).
[5] *Electron Correlations and Magnetism in Narrow Band System*, edited by T. Moriya (Springer, N.Y., 1981).
[6] J.B.Staunton and B.L.Gyorffy, Phys. Rev. Lett. **69**, 371 (1992); B.L.Gyorffy *et al.*, J. Phys. F: Met. Phys. **15**, 1337 (1985).
[7] S.Sun *et al.*, Science **287**, 1989, (2000).
[8] R.C.O'Handley, *Modern Magnetic Materials*, (Wiley, 2000).
[9] O.A.Ivanov *et al.*, Fiz. Met. Metalloved. **35**, 92, (1973)
[10] R.F.Farrow *et al.*, J. Appl. Phys. **79**, 5967, (1996).
[11] X.W.Wu *et al.*, Appl. Phys. Lett. **82**, 3475, (2003).
[12] J.-U.Thiele *et al.*, J. Appl. Phys. **91**, 6595, (2002).
[13] A.Lyberatos and K.Y.Guslienko, J. Appl. Phys. **94**, 1119, (2003).
[14] H.Saga *et al.*, Jpn. J. Appl. Phys. Part 1 **38**, 1839, (1999); M.Alex *et al.*, IEEE Trans. Magn. **37**, 1244, (2001).
[15] S.Okamoto *et al.*, Phys. Rev. B**66**, 024413, (2002).
[16] S.S.A.Razee *et al.*, Phys. Rev. B**56**, 8082 (1997).
[17] S.Ostanin *et al.*, Phys. Rev. B**69**, 064425, (2004).
[18] J.B.Staunton *et al.*,J. Phys.: Cond. Matt., in press.
[19] G.H.O.Daalderop *et al.*, Phys. Rev. B **44**, 12054 (1991); I.V.Solovyev *et al.*, Phys. Rev. B **52**, 13419 (1995); I.Galanakis, *et al.*, Phys. Rev. B **62**, 6475 (2000); P.Ravindran *et al.*, Phys. Rev. B **63**, 144409 (2001); S.D.Willoughby *et al.*, J. Appl. Phys. **91**, 8822, (2002); A.B.Shick and O.N.Mryasov, Phys. Rev. B**67**, 172407, (2003).
[20] E.Bruno and B.Ginatempo, Phys. Rev. B**55**, 12946, (1997).
[21] R.P.Feynman, Phys. Rev. **97**, 660, (1955).
[22] G.M.Stocks and H.Winter, in *The Electronic Structure of Complex Systems*, edited by S.W.Lovesey and L.Scherm, NATO-ASI Ser. B, **113**, (Plenum, New York, 1984); D.D.Johnson *et al.*, Phys. Rev. Lett. **56**, 2088, (1986).
[23] e.g. M.F.Ling *et al.*, Europhys. Lett. **25**, 631, (1994); S.S.A. Razee *et al.*, Phys. Rev. Lett. **88**, 147201, (2002); A.M.N.Niklasson *et al.*, Phys. Rev. B **67**, 235105, (2003).
[24] An Onsager cavity field technique improves this, see ref.6.